



Dealing with the surplus of glycerol production from biodiesel industry through catalytic upgrading to polyglycerols and other value-added products

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ABSTRACT

An increase in glycerol production is expected because of the increasing use of fuel additives such as methyl esters. This increase can enhance the importance of glycerol as a cheap raw material for producing value-added products. Future scenarios for worldwide glycerol market will mostly be related to the supply and demand of glycerol and its application in other industries. Much research have been developed and continuously investigated to convert low-value glycerol using different strategies and approaches. Due to the unique structure of glycerol, properties and renewability feature of it, new opportunities for the transformation of glycerol into high-valued chemicals have merged in recent years. This paper provides a review on glycerol, global market of glycerol and conversion of glycerol to value-added products. Catalytic etherification of glycerol to value-added products such as polyglycerols is particularly reviewed.

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1. Introduction

An increase in glycerol production is expected because of the increasing use of fuel additives such as methyl esters. This increase

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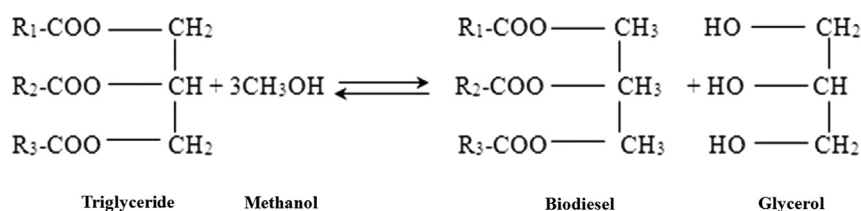


Fig. 1. Glycerol as a by-product of the methanolysis of vegetable oils.

Table 1

Typical elemental analysis results of crude glycerol from biodiesel industries [10].

Element	Weight %
Carbon (C)	52.8
Hydrogen (H)	11.1
Nitrogen (N)	< 0.0001
Sulfur (S)	–
Balance oxygen (O)	36.2

Table 2

Differences between types of glycerol [12].

Parameter	Crude glycerol	Purified glycerol	Refined/commercial glycerol
Glycerol content (%)	60–80	99.1–99.8	99.20–99.98
Moisture content (%)	1.5–6.5	0.11–0.8	0.14–0.29
Ash (%)	1.5–2.5	0.054	< 0.002
Soap (%)	3.0–5.0	0.1–0.16	0.04–0.07
Acidity (pH)	0.7–1.3	0.10–0.16	0.04–0.07
Chloride (ppm)	ND	1.0	0.6–9.5
Color (APHA)	Dark	34–45	1.8–10.3

can enhance the importance of glycerol as a cheaper raw material for new products used in surfactants, lubricants, cosmetics, food additives, etc. [1]. To deal with the major excess of glycerol and develop the “green” credentials of the compound, innovative and greener catalytic processes should be developed to convert glycerol into higher value products. The synthesis of value-added molecules from crude glycerol is an attractive replacement to disposal by incineration [2]. Fig. 1 shows the schematic of the biodiesel production through vegetable oil (triglyceride) methanolysis. Homogeneous acid and base solutions are commonly used as catalysts. In a stoichiometric reaction, 1 mole of glycerol is obtained for every 3 mole of fatty acid methyl esters (biodiesel) produced.

It is anticipated that the development of crude glycerol biorefineries benefit the economy of overall biodiesel industry through the reduction of the disposal costs of residues and increase in production of high value chemicals [3]. The process of biodiesel production starts with the purification of crude vegetable oil. The refined oil then undergoes transesterification to produce biodiesel with glycerol as the waste by-product. In a typical process, the glycerol layer (containing about 80% glycerol) [4] must be removed to enable the use of the esters as fuel. Selling of the waste glycerol solution can reduce the production cost of biodiesel by 6% [5].

Recently, biodiesel has been promoted as a means toward energy independence, rural development, and reduction of greenhouse gas emission. Biodiesel can be produced through the reaction between feedstock oil with either methanol or ethanol. The solubility of oil in methanol is less than that in ethanol. Its rate of reaction is mass transfer-limited, and methanol enables higher equilibrium conversion because of the higher reactive intermediate i.e. methoxide. Most of the biodiesel production processes use methanol, which is obtained from the petrochemical industry. This dependence on methanol can be considered a non-renewable one [6–9].

The objective of this work is to provide a review catalytic upgrading of glycerol to value-added products through etherification reaction. An overview to the relevant research topics is given in Section 1. The formation of glycerol as main by-product of biodiesel industry, investigation of the impact of this glycerol over the biodiesel production cost and glycerol market is reviewed in Section 2. This study also provides a view of transformation of this low value glycerol to upgraded products such as diglycerol using various heterogeneous catalysts as discussed in Section 3. Polyglycerols are biodegradable and biocompatible products that can be used in various industries. Various catalytic routes to produce

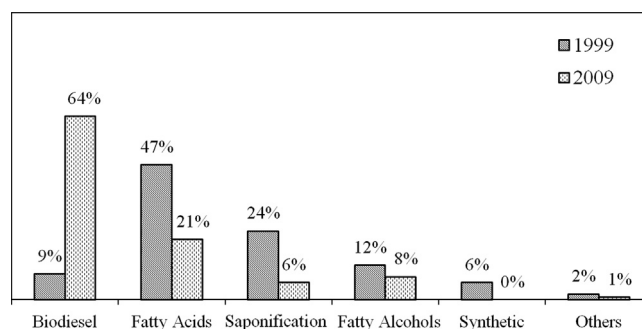


Fig. 2. Changes in glycerol supply drivers from 1999 to 2009 [14].

polyglycerols and the performance of catalysts reported in literature so far are reviewed in Section 4. Section 5 provides a review on the reaction mechanism involved in base-catalyzed etherification process.

2. Glycerol

Glycerol is a material which has numerous uses mainly because of its physical and chemical properties. Table 1 shows typical the elemental analysis results of crude glycerol produced in biodiesel industries, indicating that C, H, and O are the main elemental contents of this material [10]. Glycerol is a good renewable energy source for various applications which might be due to its high carbon content (52.8%). Furthermore, its high oxygen content (36.2%) to indicate that it is a valuable compound [11].

Glycerol can be classified into three main categories: crude, purified/refined, and commercially synthesized. Table 2 shows the major differences between these three types of glycerol from biodiesel industries. This table shows that the differences between purified and commercial glycerol are insignificant, while considerable differences can be observed between crude and purified glycerol. Actually, purified or refined glycerol is often prepared with qualities nearly equivalent to that of commercially synthesized glycerol because of its applications in sensitive fields, such as medicine, food, and cosmetics. Furthermore, Table 2 shows that

crude glycerol has about 60–80% purity, whereas purified or synthesized glycerol is generally almost 100% pure [12]. Likewise, ash, soap, and moisture could present at high quantities in crude glycerol. The acidic value of crude glycerol is slightly higher than the acidic value of the others. Its color is also darker, which may be due to the aforementioned attribute, along with some other minor impurities.

2.1. Glycerol supply drivers

A vast change has been observed among glycerol sources in the last 10 years. After 2003, changes in glycerol drivers became noticeable, at which point quick increase started until they became the largest sources in 2008. These drivers are also predicted to be the strongest future glycerol sources [13]. The fatty acid industry was considered as the main source of glycerol until 2003. However, the contribution of the said source gradually decreased, and in 2008, biodiesel became the primary glycerol source. The reason of this increasing trend of glycerol production was due to an increase in the consumption and production of biodiesel in the last few years [13].

Glycerol supply drivers shifted from one of the most popular driver i.e. the fatty acid industry, to biodiesel industry during the past 10 years, as shown in Fig. 2 [14]. From this figure, fatty acid and soap manufacturing can be seen as the two main sources of glycerol before the boom in biodiesel industry in the past few years.

In 1999, the major glycerol supply drivers were fatty acids, soaps, fatty alcohols, and biodiesel processes. The production percentages for these sources were 47%, 24%, 12% and 9%. In 2009, these sources completely changed, with the production percentages shifting to 21%, 6%, 8%, and 64%. Therefore, the biodiesel industry posed the biggest change as glycerol supply driver, from 9% to 64%, whereas fatty acid industry dropped from 47% to 21% within the same period. The increasing worldwide population may have been a factor in the increasing fuel energy consumption, i.e., increasing fuel demand. Thus, fuel energy is shifting from petroleum to biofuel to overcome this energy crisis. Biodiesel production is increasing day by day, and becoming the biggest driver of glycerol in the last few years.

2.2. Glycerol market and its oversupply problem

Until 2003, the supply of raw glycerol in the market remained relatively stable despite the start of the increase in the production of biodiesel in the United States [15]. Thereafter, the availability of crude glycerol almost doubled, but the demand remained almost unchanged. Thus, the combined effect of supply excess and limited demand of raw glycerol has led to low prices. Although pure

glycerol is an important feedstock in many industrial sectors, raw glycerol must be refined by large-scale biodiesel producers using traditional separation processes to remove impurities such as fatty acids, alcohol and catalyst. Some of these processes are filtration, chemical additions, and fractional vacuum distillation. Generally, these processes are expensive to conduct so that they are economically impossible for small- and medium-scale plants.

Since 2006, the glycerol oversupply has forced biodiesel producers to settle for raw product sale prices of 2 cents per pound or even lower. However, in mid-2007, prices were between 6 cents and 10 cents per pound [6]. In 2008, the amount of glycerol that went into annual technical applications was estimated to be approximately 160,000 t and this amount is expected to further grow at an annual rate of 2.8% [16]. Refined glycerin prices have shown a similar behavior with prices as low as 20 cents to 30 cents per pound, depending on the quality and purity [6,17]. In this sense, the raw glycerin market will continue to remain weak despite large amounts of this raw component being made available. Therefore, glycerol is a key problem in biodiesel production at present. The low sale price could convert this by-product into a residue. Thus, alternative uses must be discovered by biodiesel producers to avoid the continuous fall of glycerol price.

As the glycerol commodity market is limited to a few applications, studies suggest that any increase in biodiesel production may result in a price decline by 60% [18]. By 2016, the world biodiesel market is estimated to be at 37 billion gal. This means that every year, more than 4 billion gal of crude glycerol will be produced. The potential sale of this product could make biodiesel cheaper [19,20].

In the past few years, biodiesel production increased considerably along with the amount of residues generated during production (Fig. 3). Europe is still the largest biodiesel producer, and Brazil has the highest increase in production rate in recent years compared with the United States and Europe, that is, from 736 m³

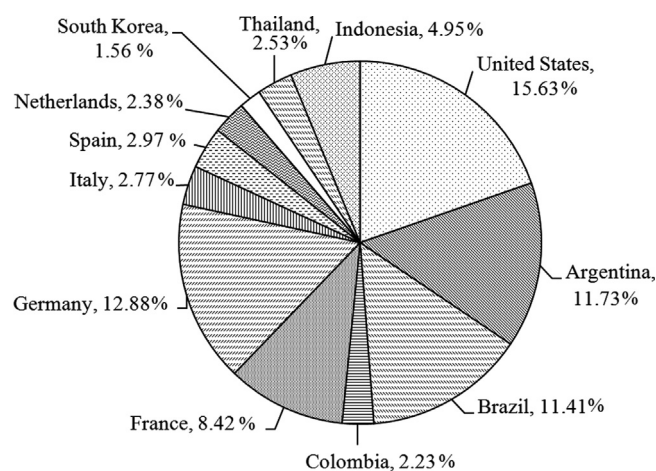


Fig. 4. Top biodiesel producing countries in 2011 [21].

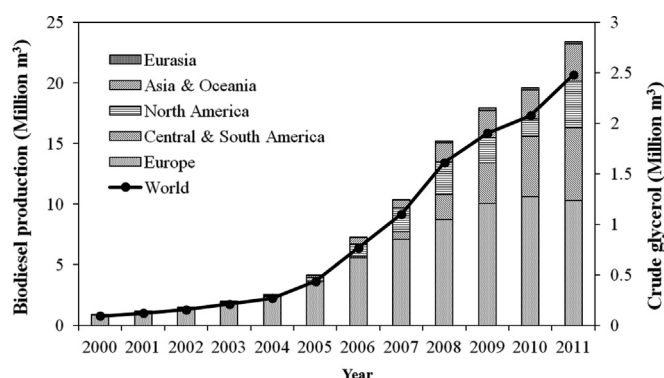


Fig. 3. World biodiesel (bars) and crude glycerol (lines) productions between 2000 and 2010 [21].

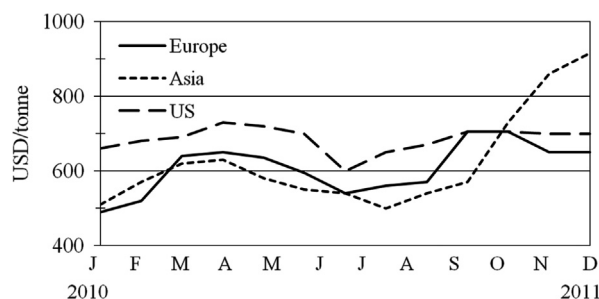


Fig. 5. Refined glycerol prices between 2010 and 2011 [26].

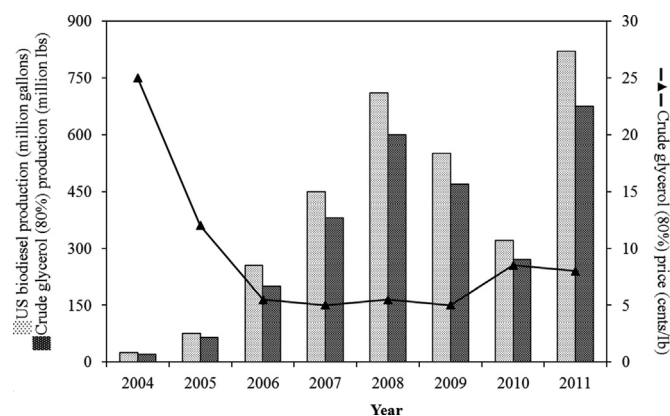


Fig. 6. US biodiesel production and crude glycerol price [36].

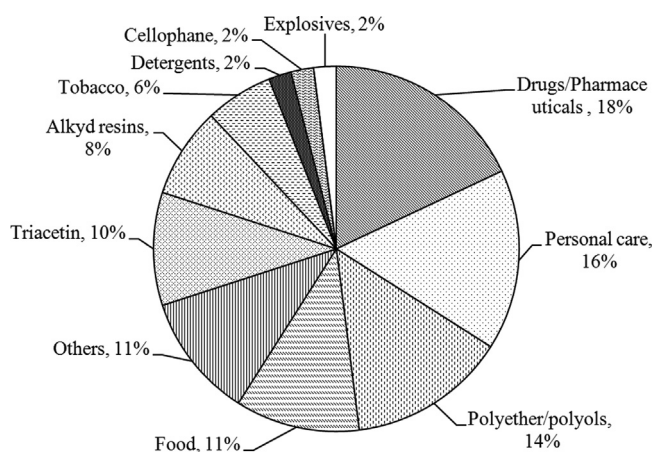


Fig. 7. Glycerol market by industry [16].

in 2005 to 2,670,000 m³ in 2011 (Fig. 4). The concentration and presence of each contaminant vary drastically from one industry to another because of the differences in the parameters, including oil source and reaction conditions. Glycerol and water content can vary from 6–92% [22] to 26–65% respectively, in crude glycerol samples [23]. The existence of these contaminations in crude glycerol samples is expected to negatively influence the bioconversion process of this co-product. However, note that the excess crude glycerol produced in the biodiesel industry leads to a decrease in glycerol prices and to the consideration of glycerol as a waste instead of a co-product [24].

2.3. Effect of glycerol price on biodiesel production cost

Currently, biodiesel production results in the rapid increase in the availability of crude glycerol worldwide. Refineries could have reached the limits of their capacity. The prices of crude glycerol have fallen down to virtually zero and even to a negative mark as producers of glycerol (particularly biodiesel) are forced to pay to have it taken away from their plants and incinerated [25].

The glycerol market is unstable as it depends on many factors such as petroleum and biodiesel production as well as its global supply and demand [26,27]. Fig. 5 shows the refined glycerol prices between 2010 and 2011 [26]. Taking the Asia market for example, the price increased from US\$ 520 to US\$ 640 per ton in the first quarter of the year 2010, and subsequently dropped to US\$ 503 per ton in August. At the beginning of 2011, glycerol price reached US\$ 858 per ton, almost twice the price in mid-2010. The

spot prices of refined glycerol in 2012 are in the range of US\$ 838–948 per ton [28]. Moreover, limited market information is available for glycerol because of its relative small scale against the global basis (approximately 1000 kt annually) [27]. The constantly changing and small markets make it difficult to predict glycerol prices in the future, resulting in the lack of reliable economic analysis of the application of glycerol. Crude glycerol has a more stable price, which is less than one-third of the cost of purified glycerol [27]. However, the downstream treatments (e.g., distillation) required to refine crude glycerol are expensive, particularly for small-scale biodiesel plants [16]. Therefore, the economic assessment of crude glycerol utilization is a challenging task.

Previous studies [29–31] show that the production cost of biodiesel varies inversely and linearly with the variations in the market value of glycerol. A report from Woo [32] indicates that the price trend of glycerol decreased over the last decade, while the production of glycerol increased because of the increase in biodiesel production. According to Fan and Burton [33], biodiesel production cost could be reduced by 25% by increasing the value of crude glycerol as its feedstock.

A promising path for the coupling of processes within a biorefinery is the employment of glycerol as a substrate for the production of biochemicals and biofuels. Glycerol is an unavoidable by-product generated in bioethanol and biodiesel production processes [34–36]. Fig. 6 shows the remarkable growth of these industries, which has led to a dramatic decrease in crude glycerol prices over the past few years [36].

These results show that the amount of crude glycerol produced as a by-product has a significant effect on the net value of the total manufacturing cost of biodiesel. However, glycerol is a valuable by-product with considerable potential as a feedstock to various value-added products. Therefore, its successful application in non-conventional uses could add a noticeable credit to the reduction of the total cost of biodiesel fuel production.

2.4. Application of biodiesel-based glycerol and its derivatives

The current market is saturated with crude glycerol because of the exponential growth of the biodiesel production. Therefore, new value-added applications of crude glycerol are being considered by biodiesel producers. The cost of converting and purifying crude glycerol into conventional materials that are applicable in food, cosmetic, or drug industries is usually high [37,38].

Glycerol has a wide range of applications, from energy bars to cough syrups and even boat coatings. According to an SDA report [10], glycerol has more than 1500 uses. Crude glycerol, resulting from biodiesel production, can be used for these applications after several purification processes. The purity of 99% or higher is used for the cosmetic and pharmaceutical markets which can be obtained by complex operation and distillation of glycerol [10]. Thus, development of new outlets for crude glycerol is essential for the present and future markets. Equally important is the development of more sustainable refining processes and more economical plants.

With respect to the research and development of new applications of glycerol, industries generally hope to increase crude glycerol prices [39]. The success of large-scale utilization of glycerol can assure the stability of the market and the increase in price [40]. The glycerol market will be stronger with the introduction of new applications of crude glycerol and these new usages may indirectly support the reduction of biodiesel production cost. Other opportunities to explore the most valuable applications of crude glycerol are available [41]. These opportunities can boost biodiesel production and transform crude glycerol into a vital part of renewable energy [24,42–46].

Establishing the new outlets for the glycerol may increase the price of crude glycerol. If new outlets for glycerol, specifically

crude glycerol is unsuccessful, glycerol prices will continue to lag. As a result, surplus amount of crude glycerol may be sold as a waste product or may be used only in incinerators to heat industrial boilers [42,47]. Nevertheless, glycerol is a main chemical compound in the world economy. Therefore, new prospects for the glycerol industry should be continuously ventured into to help in improving the economics of biodiesel production.

Glycerol is traditionally used either as food, tobacco, and drug additive or as raw material in the synthesis of trinitroglycerine, alkyd resins, and polyurethanes [16]. The usage of low-grade quality glycerol obtained from biodiesel production is a huge challenge because this type of glycerol cannot be used for food and cosmetic purposes without further purification. An effective use or conversion of crude glycerol into specific products will decrease the biodiesel production costs [48].

The oleochemical industry is a major source of glycerol. The process requires fat splitting of glycerides and biofuels such as biodiesel [49]. The widespread use of glycerol in the cosmetic, soap, pharmaceutical, food, and tobacco industries is shown in Fig. 7 [16]. In the glycerol pharmaceutical market, toothpaste and cosmetics account for 28%, tobacco for 15%, foodstuff for 13%, and manufacture of urethanes for 11%. The remainder is used in the manufacture of lacquers, varnishes, inks, adhesives, synthetic plastics, regenerated cellulose, explosives, and other industrial uses. Furthermore, glycerol is increasingly used as a substitute for propylene glycol [50]. Therefore, glycerol has become a popular research topic, and researchers are keen on discovering alternate applications in fuels and chemicals [51–53].

The required purity is a deterrent future in the use of glycerol from biodiesel production in pharmaceuticals and cosmetics. However, several factors such as low price, availability, and functionalities make glycerol an attractive choice for various industrial processes. Developing selective glycerol-based catalytic processes has become a major challenge as suggested by the high number of patents and research papers being published about it [54,55].

The purification of glycerol using the distillation method is a costly process, and the low price of glycerol makes it uneconomical [56]. Moreover, glycerol exhibits low volatility due to its high boiling point (290 °C), and it does not directly burn in either petrol or diesel engine [18]. Consequently, the idea of converting glycerol into value-added products becomes attractive because it presents a tremendous opportunity for the biodiesel industry to increase revenue and expand its product market.

3. Polyglycerols

Polyglycerol is a highly branched polyol that is clear and viscous, highly soluble in water and in other polar organic solvents such as methanol, and essentially non-volatile at room temperature [57]. At room temperature, polyglycerol is highly viscous, and the viscosity increases with molecular weight. Its high compound functionality combined with the versatile and well-investigated reactivity of hydroxyl groups forms the basis for a variety of derivatives. A number of polyglycerols are commercially available for different applications, ranging from cosmetics to controlled drug release [58,59].

Biocompatibility is an attractive feature of aliphatic polyether structures containing hydroxyl end-groups, including polyglycerols or linear polyethylene glycerols (PEGs), which are approved for a wide variety of medical and biomedical applications. Controlled etherification of glycerol to form polyglycerols with a narrow molecular weight distribution in the range of 1000–30,000 g/mol is done through the anionic polymerization of glycidol in rapid cation exchange equilibrium. Partial esterification of polyglycerols with fatty acids yields amphiphilic materials that behave as nanocapsules [57]. Linkage of individual glycerol monomers to obtain polyglycerol is one of the routes that can be used to physically upgrade the structure of glycerol. Branched isomers are created from secondary hydroxyls, whereas cyclic isomers result from the intramolecular condensation of the previous ones [60].

In several previous articles [1,61–63], producing oligomers using the transformation of glycerol is referred to as etherification. Often, oligomers with 2–4 glycerol units are viewed as polyglycerols, without a strict differentiation as to where the oligomers end and the polyglycerol begins, while bearing the inherent possibility of confusion with high-molecular weight, branched polyglycerol produced through anionic polymerization [64].

Table 3 shows the variations in the physical properties of glycerol and its higher oligomers [65]. Generally, with increasing oligomer molecular weight, the density correspondingly increases with the addition of glycerol units in the chain. The ability to break ether bonds is also more difficult due to the effects of chain structure. Thus, the correlation between pressure and temperature must be considered. Hydroxyl number can be measured experimentally and is defined as the amount of KOH (mg) equivalent to the hydroxyl content of 1 g of sample. The hydroxyl number generally decreases with increasing number of glycerol units, which also results in variations to polarity, solubility, viscosity and color (from water clear to dark yellow) [65,66].

3.1. Diglycerol

Diglycerol (DG) is a clear viscous liquid and very similar to glycerol, but with higher molecular weight and less volatility. DG is water soluble and can be combined with aqueous systems. Table 4 compares the physico-chemical properties of DG and glycerol, which are important in understanding the behavior of DG to explain its kinetic activity in the etherification reaction [67]. The properties of DG are more desirable compared with glycerol. In addition, DG products are conferred with properties that are more applicable and valuable for use in many applications.

Diglycerol is envisaged to be the most plentiful product formed from a pool of isomers during the reaction. Linear, branched, and cyclic dimers are formed, and their formation depends on the location of the interacting hydroxyl groups from different individual monomers. Coupling of primary to primary, primary to secondary, and secondary to secondary locations, as well as second-generation etherification products, results in the formation of prim–prim, prim–sec, sec–sec, and cyclic dimers, respectively [68]. The dimension and basal spacing value (d) of each dimer are shown in Fig. 8 [69].

Table 3
Physical data of glycerol, diglycerol and higher oligomers [65].

Name	Molecular formula/weight (g/mol)	Refractivity n_D^{20} (–)	Density (g/cm ³)	Boiling point (°C)/(Pa)	Hydroxyl number (mg KOH/g)
Glycerol	C ₃ H ₈ O ₃ 92	1.4720	1.2560	290	1830
Diglycerol	C ₆ H ₁₄ O ₅ 166	1.4897	1.2790	205/133	1352
Triglycerol	C ₉ H ₂₀ O ₇ 240	1.4901 (40 °C)	1.2646 (40 °C)	> 250/13.3	1169
Tetraglycerol	C ₁₃ H ₂₆ O ₉ 314	1.4940 (40 °C)	1.2687 (40 °C)	69–73 (melting point)	1071

Table 4
Physico-chemical properties of glycerol and diglycerol [67].

Property	Unit	Diglycerol	Glycerol
Molecular formula	–	C ₆ H ₁₄ O ₅	C ₃ H ₈ O ₃
Molecular weight	g/mol	166	92
Density	g/ml	1.276	1.256
Dynamic viscosity	Pa s	13	1
Refractive index	–	1.487	1.472
Dielectric constant	–	34	46
Boiling point	°C	205 (1.3 mbar)	290
Heat of dissolution in water	J/g	–52	–62
Specific heat capacity	J/g K	2.28	2.38
Thermal conductivity	Wm K	0.28	0.29
Thermal expansion coefficient	°C	0.00053 (20–60 °C)	0.00052 (20–60 °C)
Flash point	°C	230	199
Fire point	°C	264	204
Autoignition	°C	380	370

3.2. Application of polyglycerol

In the current polyglycerol market, this product generally includes different oligomer mixtures such as diglycerol, triglycerol, tetraglycerol, hexaglycerol and decaglycerol. Polyglycerols can be transformed to polyglycerol esters to use as an emulsifier in the cosmetic/food and plastic industries. A main potential market for polyglycerol is polyglycerol ester which can be used as non-ionic surfactant. Due to the amphiphilic character of polyglycerols, these materials are capable to be used in the stabilization of different suspensions and emulsions [70].

Polyglycerols are used to control viscosity, emulsify and stabilize product formulae. They are incorporated into moisturizing sunscreens, sun protective sticks, hair-styling gels, long-acting hand creams, skin treatment gels, skin cleansers and baby creams. In the food industry, polyglycerol esters are used as emulsifying agents in the production of fine bakery products, fat replacement products and chewing gum [70].

In 2012, natural emulsifiers accounted for about one-third of the total emulsifier market, whereas synthetic emulsifiers held the rest. Among the synthetic segment, di-glycerides and derivatives constitute the largest share and are expected to grow at a modest pace. Other synthetic emulsifier which comprises of polyglycerol esters, sucrose esters and polyglycerol polyricinoleate (PGPR) is expected to drive the market for emulsifiers. However, palm oil and other vegetable oil prices are highly volatile and ascertaining accurate future prices would be difficult [71].

Europe generated maximum revenue in global food emulsifier market. The U.S., however, is the leader in the segment in the global market. North America, hence, is the second largest market of the segment. China drives the Asia-Pacific market with the highest annual growth rate globally. Germany generated maximum revenue in European market, followed by Italy. ROW emulsifier market, led by Brazil, is also given a boost by the promising growth in South Africa and Middle East [71].

According to a new market research report [71], “Food Emulsifiers Market By Types (Mono, Di-Glycerides and Derivatives, Lecithin, Sorbitan Esters, Stearoyl Lactylates and Others), Applications (Bakery & Confectionery, Convenience Foods, Dairy Products, Meat Products and Others) and Geography – Global Trends and Forecast To 2018”, published by Markets and Markets [71], the food emulsifiers market will grow from an estimated level of \$ 2108.9 million in 2012 to \$ 2858.6 million by 2018 with an annual growth rate of 5.2% from 2013 to 2018. Europe led the global market followed by North America and Asia-Pacific in terms of revenue in the year 2012.

3.3. Production of diglycerol

Different methods or routes can be used to synthesize pure diglycerol, either from glycerol itself or from other substances. In laboratory-scale production, direct synthesis routes were described by Wittcoff et al. [72,73]. Fig. 9 shows several conventional processes for diglycerol synthesis.

All reported processes thus far have the disadvantage of requiring the use of starting substances that are difficult to obtain or synthesis procedures that require several intermediate steps that produces great amounts of salts as by-products [66]. Such methods mostly consist of non-catalytic processes involving allylation, hydroxylation, and hydrolysis. In thermal conversion of glycerol, the reaction is generally performed at specified temperatures under an inert protecting atmosphere [65]. A purely thermal conversion without the addition of a catalyst is set above 200 °C; at 290 °C in the dark, strongly smelling products are formed. At low temperature (180 °C) and in the presence of alkaline, only a small amount of diglycerol is formed with a low conversion degree. Traces of oxygen that present could result in the formation of acrolein and other condensation products. Thus, air should be eliminated from the system during the reaction [74].

During the basic hydrolysis of epichlorohydrin 10 (Fig. 8) by NaOH, an intermediary glycidol 11 is assumed to form aside from glycerol 8, and this intermediary reacts with non-converted 10 or 8 to form diglycerol 1. The residual glycerol has to be separated and water should be removed from raw diglycerol. The reactions of glycidol or epichlorohydrin with glycerol similarly exhibit coupling of the OH groups that is not confined to the terminal positions, with the middle OH groups being involved as well. These events lead to the formation of α , β - and β , β' -diglycerol, aside from α , α' -diglycerol [65,66,75].

Methods of catalyzed glycerol oligomerization have been developed. The process of synthesizing diglycerol has also improved with the application of simple processing techniques, including the use of affordable materials and equipment. Many studies on these catalysts, as well as the improvement of catalytic reactions, have been done. Such works include the study on homogeneous and heterogeneous acid or basic catalysts. The highlights of this related topic in the etherification reaction will be discussed in the following section.

4. Processes used to produce value-added products from glycerol

The superiority of biodiesel over petroleum products with regard to health and environmental concerns (i.e., no sulfur content; low harmful emission of particulate matter, HC, CO, etc.; and better CO₂ lifecycle for global warming alleviation), as well as to engine performance, has encouraged Asian countries to use biodiesel as an alternative fuel source and as an innovative solution to curb the air pollution caused by the growing number of vehicles in the population. In recent years, the availability of glycerol has significantly increased because of the immense growth in biodiesel production [63], with glycerol formation equivalent to 10 wt% of the total biodiesel produced [76]. This development has resulted in a glycerol surplus, which has considerably affected the glycerol market and caused extreme decrease in glycerol prices [77]. The conversion of surplus glycerol to value-added chemicals is important [78,79]. To tackle excess glycerol obtained from vegetable oil transesterification and to build on the green credentials of the compound, a new, innovative, and greener catalytic process that can transform glycerol into high-value products is required [79].

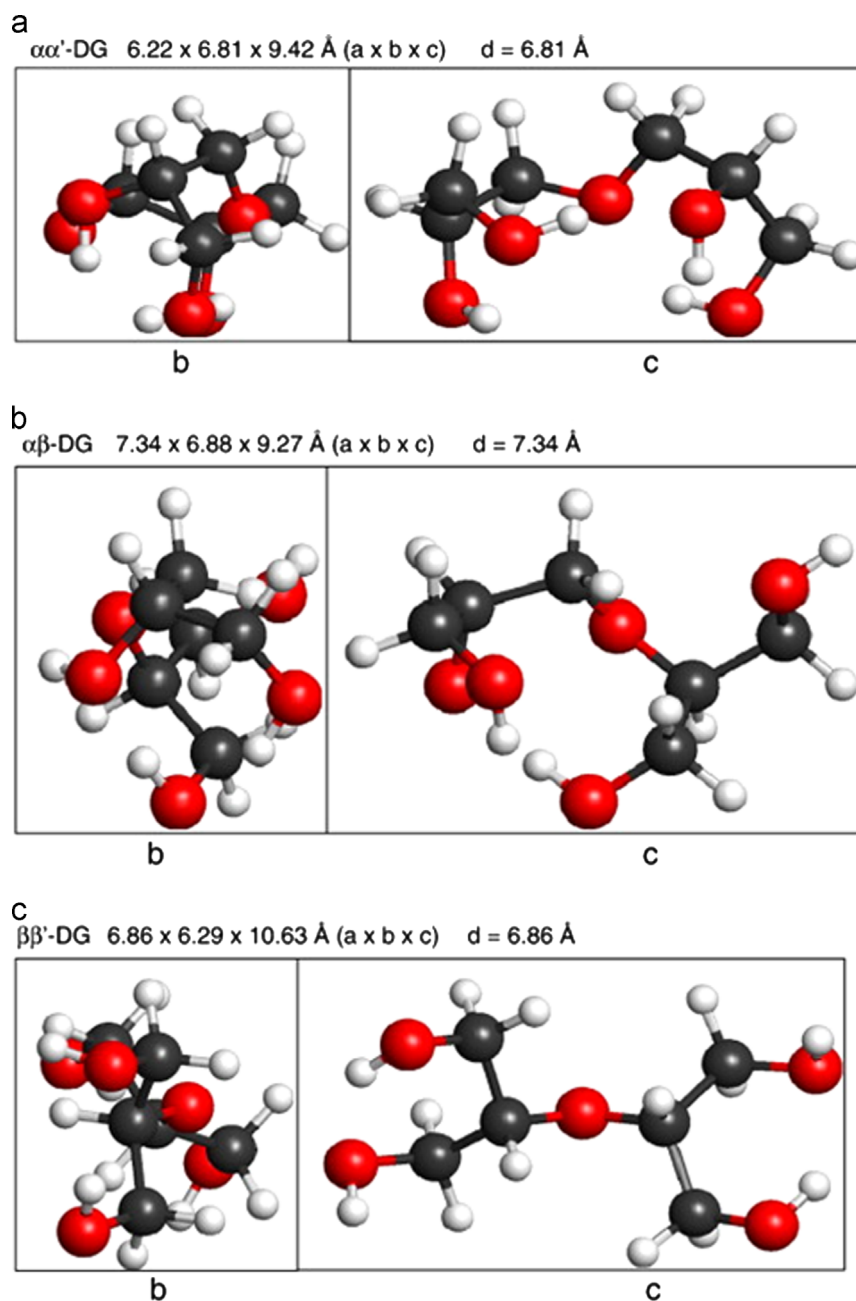


Fig. 8. Spatial properties of the three constitutional diglycerol isomers ($\alpha\alpha'$, $\alpha\beta$, $\beta\beta'$) [69].

Investigating processes with glycerol as a raw material necessitates knowledge on fundamental industrial processes, such as oxidation, hydrogenation, hydrolysis, chlorination, etherification and esterification [80–85]. Most of the products manufactured from glycerol are based on unmodified glycerol or modified glycerol molecules when the production of more complex chemical compounds has become too costly. However, with abundant glycerol in the commodity market, this compound could potentially be used in manufacturing polymers, ethers, and other fine chemicals.

One of the possibilities for converting glycerol into a value-added product is its conversion to acrolein, which is used in many fine chemical products. Catalytic dehydration of glycerol offers an alternative route to the production of acrolein. The said glycerol derivative is a versatile intermediate used in the synthesis of pharmaceuticals, detergents, and polymers [86]. Polyglycerol is a useful derivative of glycerol, which is extensively employed in

controlled drug release and cosmetics. This derivative comprises several units of glycerol that form a branched ether structure with terminal hydroxyl groups [87,88]. The multifunctional structure and properties of glycerol allows it to be easily converted into various products through different reaction pathways. This process was comprehensively reviewed recently [18,84,85].

To utilize excess glycerol produced from biodiesel production, industries are developing innovative methods that can use glycerol as a building block for the production of value added chemicals. The use of glycerol provides a promising possibility of being independent from fossil fuels. However, reports show the cost competitiveness between petroleum-derived products and products obtained from glycerol [84]. The balance can only be maintained when the cost price of glycerol is significantly lower than that of its petroleum-based counterparts. The unique structure of glycerol makes it possible to conduct a heterogeneous

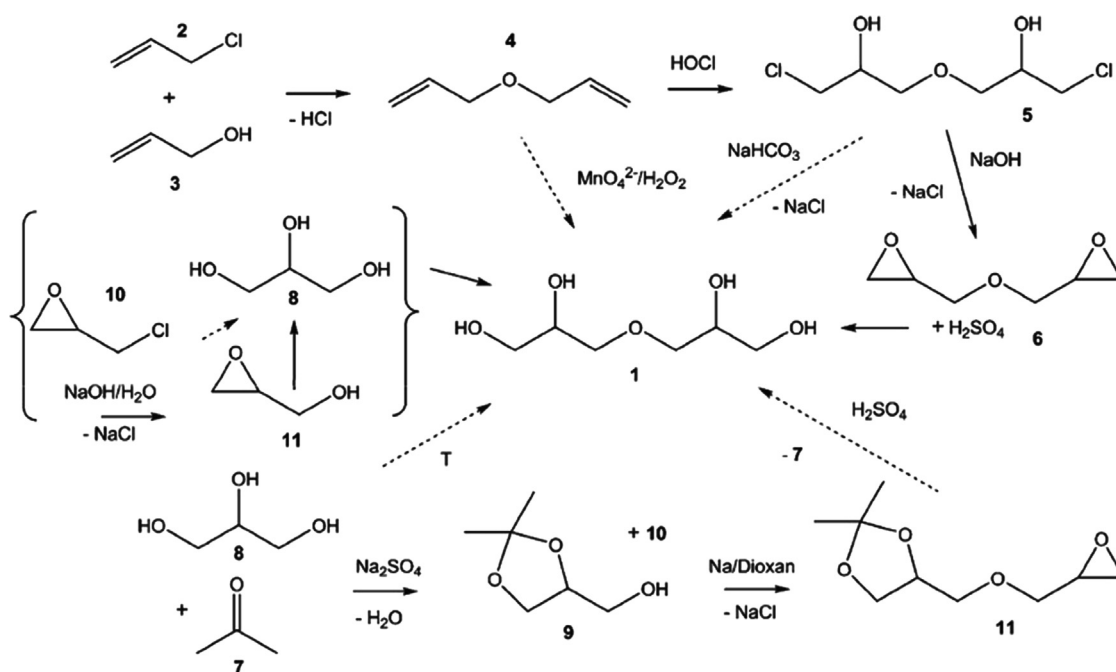


Fig. 9. Different synthesis routes of diglycerol [65].

catalytic oxidation reaction using a cheaper oxidizing agent such as air, oxygen, and hydrogen peroxide [89].

The catalytic transformation of glycerol into various chemicals by hydrogenolysis [80,90–93], polymerization [66,94], etherification [95–98], oxidation [99–101], dehydration [86,102,103], acetylation [84,104], and transesterification [105–107] has been reported. Of these processes, etherification is the most promising option because it can directly yield compounds that can be used as fuel additives [108]. Moreover, they can also be used as intermediates in the pharmaceutical industry, agrochemicals, and non-ionic surfactants [1].

Much research have been developed and continuously investigated to transform low-value glycerol using different strategies and approaches. To help make biodiesel plants more profitable, converting glycerol into chemical commodities of higher price and larger market is desirable. Generally, the conversion of glycerol can be broken down into two classes: (1) oxidation or reduction of glycerol into other three carbon compounds and (2) reaction of glycerol with other molecules to form new species. As the first step, a product with a sufficiently large market was chosen that can absorb the added glycerol to impose a higher price [109]. For a quick understanding of what that can be done to crude glycerol, its derivative products along with their corresponding methods/processes are summarized in Table 5. This listing may be helpful for biodiesel technocrats, giving them a choice for which compound they want to go for in place of crude glycerol.

Various heterogeneous catalysts have been employed in the etherification process [17,63,77,79,110–113]. Heterogeneous catalysts can be acidic or basic in nature. The use of acidic catalyst, in which the reaction products formed are cyclic polyglycerols, has several disadvantages. Deterioration of product quality will occur because of the secondary reactions produced, such as dehydration and oxidation of the intermediate product. Although the conversion of the reaction is relatively higher and faster, the selectivity remains low. Thus, the use of a basic rather than an acidic catalyst is preferred, as the product is more selective (avoids higher oligomers) and shows higher etherification activity. The basic catalysis of glycerol seems to be effective, as the product is more selective and possesses a high degree of conversion.

The etherification process proceeds through the stepwise reaction between the functional reactant groups. The size of polymer molecules increases at a relatively slow pace in such polymerization processes. One proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on until, eventually, large-sized polymer molecules are formed. Step polymerization can be distinguished from chain polymerization by the reaction occurring between any of the different-sized species present in the reaction system [114].

The linkage of individual glycerol monomers in the etherification reaction will create one molecule of water as a side product. This reaction confers certain changes in the physical properties of glycerol, making it more viscous, causing color change from water clear to dark yellow, and affecting polarity. With increasing molecular weight, the hydroxyl number (diglycerol with 4 hydroxyls, triglycerol 5, tetraglycerol 6, etc.) decreases. This increase causes a change in the polarity of oligomers, that is, low oligomers are more hydrophilic than higher ones so that they have better solubility in polar solvents such as water. The viscosity increases with higher degree of oligomerization, often accompanied by a color change from water clear (glycerol) to dark yellow. Presumably, this coloration occurs due to dehydration side-reactions [66].

In etherification, glycerol can be converted into branched, oxygen-containing components through the reaction with either alcohols or alkenes. The reaction products could potentially be used as valuable fuel additives, such as *tert*-butyl ethers. Acidic homogenous catalysts and heterogeneous catalysts such as zeolites can be employed in this process. Karinen and Krause [115] reported that liquid-phase etherification of glycerol with isobutene in the presence of an acidic ion-exchange resin catalyst can yield up to five ether products, with side products in the form of C8 to C16 hydrocarbons.

4.1. Catalytic etherification

Glycerol etherification with or without organic solvents has been intensively studied using different homogeneous alkali catalysts such as hydroxides and carbonates. Recently, research

Table 5

Derivative products from glycerol along with their corresponding production methods.

Product name	Process method/nature	Reference
1,3-Propanediol	Selective hydroxylation technique involving three stages of acetalization, tosylation, and detosylation. Dehydroxylation of glycerol to 1,3-propanediol over a Pt/WO ₃ /ZrO ₂ catalyst Pt/WO ₃ /TiO ₂ /SiO ₂ catalyst in aqueous media. Batch and continuous microbial fermentations by <i>Clostridium butyricum</i> , <i>Citrobacter freundii</i> . <i>Klebsiella pneumoniae</i> . The cultures are specified by nutrient. Microbial and glycerol concentrations. The key parameters are temperature, time and pH.	[110]. [90,111] [112] [113,114] [115] [113,116] [113,117]
Hydrogen	Steam reforming of glycerol in the gas with Group 8–10 metal catalysts. Catalytic steam reforming of glycerol using a commercial Ni-based catalyst. Calcined dolomite sorbent and calcium oxide sorbent, in a continuous flow fixed-bed reactor. Microbial fermentation of glycerol by <i>Enterobacter aerogenes</i> HU-101, in a continuous packed-bed reactor. Hydrogen production from glycerol using microbial electrolysis cells (MECs). Hydrogen production from steam-glycerol reforming, the results show that high temperature, low pressure, low feeding reactants to inert gas ratio and low gas flow rate are favorable for steam reforming of glycerol for hydrogen production. There is an optimal water to glycerol feed ratio for steam reforming of glycerol for hydrogen production which is about 9.0. Hydrogen production via glycerol steam reforming with CO ₂ . Production of renewable hydrogen from aqueous-phase reforming of glycerol over Pt-based catalysts supported on different oxides (Al ₂ O ₃ , ZrO ₂ , MgO and CeO ₂). Production of hydrogen from steam reforming of glycerol using nickel catalysts supported on Al ₂ O ₃ , CeO ₂ and ZrO ₂ . Production of hydrogen from steam reforming of glycerol using Pt-based catalysts supported on Al ₂ O ₃ , SiO ₂ , AC, MgO, HUSY, and SAPO-11. Aqueous-phase reforming of biomass-derived oxygenated hydrocarbons over a tin-promoted Raney-nickel catalyst.	[118] [119,120] [119] [121] [122] [123] [124,125] [126] [127] [128] [129] [130]
Succinic acid	Bacterial fermentation use of several promising succinic acid producers including <i>Actinobacillus succinogenes</i> , <i>Anaerobiospirillum succiniciproducens</i> , <i>Mannheimia succiniciproducens</i> and recombinant <i>Escherichia coli</i> .	[131]
1,2-Propanediol	Glycerol hydrogenolysis over the Ru/C catalyst using an ion-exchange resin. Dehydration–hydrogenation of glycerol at ambient hydrogen pressure over supported copper metal catalysts. Aqueous phase hydrogenolysis of glycerol catalyzed by an admixture of 5 wt% Ru/Al ₂ O ₃ and 5 wt% Pt/Al ₂ O ₃ catalysts, without external hydrogen addition. Hydrogenolysis of glycerol using bi-functional Co/MgO catalysts, where the solid MgO acts as the basic component and the support of cobalt nanoparticles. Low-pressure hydrogenolysis of glycerol to propylene glycol using nickel, palladium, platinum, copper, and copper-chromite catalysts. Selective hydrogenolysis with Raney nickel catalyst in an autoclave with hydrogen.	[132,133] [134] [135] [136] [137] [138]
Dihydroxyacetone (DHA)	Overexpression of glycerol dehydrogenase in an alcohol dehydrogenase-deficient (ADH-deficient) mutant of <i>Gluconobacter oxydans</i> . Bioconversion of glycerol with immobilized <i>Gluconobacter oxydans</i> cell in the air-lift reactor. Chemoselective catalytic oxidation with Air on platinum metals. Selective oxidation of glycerol with platinum–bismuth (BiPt) catalyst. Microbial fermentation of DHA by <i>Gluconobacter oxydans</i> in a semi-continuous two-stage repeated fed-batch process.	[131] [121] [51] [116] [116]
Polyesters	Reacting glycerol and aliphatic dicarboxylic acids of various length. Synthesis and characterization of elastic aliphatic polyesters from sebacic acid, glycol and glycerol through a two-step process. Reacting glycerol and adipic acid without any solvents in the presence of tin catalysts.	[131] [121] [111]
Polyglycerols	Etherification of glycerol over MgAl mixed oxides without solvent in a batch reactor Selective etherification of glycerol over impregnated basic MCM-41 type mesoporous catalysts.	[127] [1]
Polyhydroxyalkan-oates (PHAs)	Submerged and solid-state fermentation processes using inexpensive carbon sources (from waste materials and by-products). Fermentation of hydrolyzed whey permeate and glycerol liquid phase using a highly osmophilic organism (production of polyhydroxyalkanoates from agricultural waste and surplus materials).	[121] [131]

attention has been shifted toward heterogeneous catalysts such as zeolites, mesoporous silica, and metal oxides [76,79,116].

Chemical reaction takes place on the active sites on the catalyst surface. For the reaction to occur, one or more reactants must diffuse to the catalyst surface and adsorb onto the surface. After the reaction, the products must desorb from the surface and diffuse from the solid surface. This transport of reactants and products from one phase to another frequently has a significant role in limiting the reaction rate.

To find the suitable catalysts for the etherification of polyhydroxy compounds, particularly of glycerol and ethylene glycol, optimization of reaction conditions and procedure has been a subject of several patents. Glycerol etherification by isobutylene established by Behr and Obenorf [117] and homogeneous and heterogeneous catalysts for glycerol etherification were studied. The commercial strong acid ion-exchange resin Amberlyst 15 have shown the best results among heterogeneous catalysts and the best homogeneous catalyst was p-toluenesulfonic acid. The change in concentration with the time at which the individual

components were reacted in the mixture was evaluated by the simplified kinetic model, considering only the main reactions that lead to ether formation.

Klepáčová et al. [118] discussed in detail the study of catalytic activity and selectivity of ion-exchange resins of Amberlyst type and large-pore zeolites on tert-butylation of glycerol with isobutylene and tert-butyl alcohol. Glycerol condensation (etherification) was studied in the presence of alkaline exchange zeolites and mesoporous basic catalysts. The selectivity of diglycerol increased when X zeolites were exchanged with cesium, whereas the selectivity of Cs-ZSM5 was comparable to that of Na₂CO₃. Over mesoporous M-La or M-Mn materials, the formation of triglycerol and tetraglycerol was more significant. Such results could be due to the changes in both pore size and basicity of the catalysts [61].

Glycerol etherification involves polyglycerols, which are oxygenated compounds used as surfactants, lubricants, cosmetics, and food preservatives. Polyglycerols have a low level of polymerization that can be obtained in linear, cyclic, and branched chains. However, research efforts have been focused on selective

production of di- and/or tri-glycerols. The selectivity of glycerol etherification is like pseudo-polymerization, where a mixture of lineal and cyclic polyglycerols is generally obtained, particularly in the presence of homogeneous catalysts, such as sodium, potassium and carbonate hydroxide [60]. Etherification selectivity in the first reaction step of acid catalysts was not controlled, and thus, resulted in a mixture of di- to hexa-glycerols (lineal or cyclic), polyglycerol esters, and acrolein as by-products. Nonetheless, selectivity in the first step could be slightly improved by modifying the pseudo-pore size in the mesoporous materials [1]. Likewise, Na_2CO_3 improved glycerol conversion, although low selectivities with regard to di- and tri-glycerols were obtained. Subsequently, alkaline exchange zeolites were studied, and selectivity was increased [60]. The incorporation of elements such as Al, Mg, and La on mesoporous catalytic structure modified only the activity, and selectivity was set to be almost constant. Clacens et al. [1] found that other methods of impregnation method produced materials that were more stable and selective than incorporation. Among the impregnated materials, La was most active but it had the worst selectivity. In contrast, a positive behavior was observed in Mg, which was highly selective.

Solid catalysts are good alternatives for homogeneous catalysts in the etherification of glycerol to produce polyglycerol because the former do not dissolve in the reactant mixture, thus eliminating the separation issues associated with the conventional homogeneous process. However, the removal of homogeneous catalysts is technically difficult because this process produces a large amount of wastewater that needs to be treated via neutralization. In the near future, conventional homogeneous catalysts are expected to be replaced with solid catalysts due to economic and environmental reasons [119,120].

The advantages of heterogeneous catalysts include low cost, reusability, possibility of recovery after the reaction process, and easy separation from the reaction [121,122]. Moreover, heterogeneous catalysts can be designed to provide higher activity and selectivity, eliminate corrosion problems, and improve thermal stability; they have low diffusion resistance (for highly porous materials) and generally longer lifetime [123,124].

Conventional methods for polyglycerol synthesis remain difficult because this reaction requires drastic conditions, namely, high reaction temperature and caustic environment [60]. For example, the use of Na_2CO_3 as a homogeneous catalyst results in high conversion but quite low selectivity. Additionally, several steps that include filtration, purification, and neutralization are required to recover almost pure diglycerol [66]. This procedure produces large amounts of basic aqueous waste which are environmentally damaging [61]. Therefore, for this important catalytic process, heterogeneous catalysts that are highly active, selective, and stable must be identified. Although most research studies conducted in this field are patented, some are reported in open literature.

4.2. Acid catalyzed etherification of glycerol

The glycerol will convert to various products of glycerol ether. In these reactions, the reaction occurs very fast and conversion is usually high. Usually, within 2 h, approximately all glycerol can be converted to products [69]. The non-selective product is formed due to the high-reaction temperature that favors the dehydration of primary oligomer to produce higher oligomers. Homogeneous catalyst has a rapid reaction rate which causes fast depletion of glycerol while being used to create higher oligomers [69]. Moreover, the color of the ether product obtained from the acid-catalyzed etherification shows its quality. When the product deteriorated and secondary product such as cyclic glycerol created, a dark and cloudy color could be observed [65,69].

Acid catalytic etherification is upgraded by changing homogeneous with heterogeneous acid catalysts. The use of a reactant and a catalyst in different phases is very interesting. Utilization of modified zeolite beta, MCM-41 and Amberlyst 16 as catalysts in glycerol etherification studied has been reported recently [125]. By using zeolite beta at various Si/Al molar ratios different products formed such as linear diglycerol, cyclic diglycerol, cyclic triglycerol and higher oligomers.

Further investigation on the performance of the acid catalyst included the use of MCM-41 as a catalyst [126]. For this particular catalyst, the production of higher oligomers was successfully supported, thus representing better selectivity to diglycerol. However, the conversion of glycerol was still low for MCM-41. The structure and the better porous system that are offered by MCM-41 allowed glycerol to access the internal pores to undergo reaction. This porous structure of MCM-41 was responsible for the increase of diglycerol formation and the large porous structure in meso-size range allowed fast internal diffusion of reactants and products.

4.3. Base catalyzed etherification of glycerol

The role of bases as active sites in enhancing the etherification reaction and improvement of catalyst performance has been investigated and several series of homogeneous and heterogeneous basic catalysts have been identified in previous studies. Several bases have been examined as homogeneous catalysts for the conversion of glycerol to polyglycerols. Oxides such as ZnO , MgO , and CaO are less active in the aforementioned reaction due to solubility issues. Nevertheless, these reactions are often not sufficiently fast (in terms of glycerol conversion) or do not selectively produce DG apart from difficulties in filtration, neutralization, and product purification [61]. Aslan [127] reported that 96% glycerol conversion with a corresponding selectivity to DG of 24% was achieved using 2% Na_2CO_3 catalyst at 260 °C for 24 h. Alkaline metals impregnated into mesoporous catalysts were reported to achieve 80% conversion of glycerol with a selectivity to DG of no less than 40% at 260 °C and a long reaction period of 24 h [1]. In 2005, the use of zeolitic catalysts for glycerol etherification was attempted and it resulted in 80% glycerol conversion and less than 20% selectivity to DG at 260 °C [128]. Recently, glycerol etherification was performed using Mg Al mixed oxide catalyst at a lower reaction temperature of 220 °C. For this mixed oxide catalyst, a maximum conversion of 50% was recorded with a high selectivity to DG of approximately 90% after 24 h [129]. Evidently, different catalysts demonstrate different activities and capacities to produce the desired product.

Further theoretical studies of alkaline earth metals have been focused on the role of surface basicity and Lewis acidity of the catalyst. The catalytic behavior of metal oxide surfaces are often explained by the acid/base characteristics [130]. Generally, for acid/base characterizations of surface sites on oxides the adsorption of probe molecules, such as ammonia, pyridine and carbon dioxide is used, and these characterizations usually have been used to explain the catalytic behavior of oxide surfaces. The nature of acidic and basic sites on oxide surfaces can be described in Lewis and Brønsted terms. On metal oxides, coordinated unsaturated metal cations are generally considered as Lewis acid sites, whereas the oxygen anions are regarded as Lewis base sites [131,132]. The electron-deficient metal cations exhibit acidic, electron-acceptor characteristics, whereas the electron-rich oxygen anions exhibit basic, electron-donor characteristics [131].

Alkali-modified zeolites, MCM-41 silica materials and alkaline earth-based mesoporous solids were studied, and partial or complete collapse of the porous structure were observed for all these catalysts [133]. The structural collapse can be resolved through grafting

Table 6
Operating conditions of glycerol etherification process using different catalysts.

Catalyst	Glycerol conversion	Selectivity	Reaction conditions	Ref.
Cs impregnated MCM-41	80%	Diglycerol: 75% Triglycerol: 25%	Glycerol etherification is carried out at 260 °C in a batch reactor at atmospheric pressure under N ₂ in the presence of 2 wt% of catalyst.	[62]
La incorporated MCM-41	90%	Diglycerol: 40% Triglycerol: 23%		
Cs exchanged X zeolite	80%	Diglycerol: 65% Triglycerol: 20%		
CsZSM-5(Si/Me ratio: 1000)	13%	Diglycerol: 100% Triglycerol: 0%	Selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalysts, homogeneous and modified zeolite catalysts, 8 h, 260 °C.	[1]
CsZSM-5 (Si/Me ratio: 1000)	12%	Diglycerol: 94% Triglycerol: 6%		
CsX (impregnated)	36%	Diglycerol: 88% Triglycerol: 12%		
CsX (exchanged)	51%	Diglycerol: 83% Triglycerol: 17%		
Heterogeneous (Cs ₂₅ Al(20))	80%	Diglycerol: 55% Triglycerol: 25%	Heterogeneous, 15 h, 260 °C.	
MgAl–Na	50%	Diglycerol: 85% Triglycerol: 15%	Etherification of glycerol to polyglycerols over MgAl mixed oxides, glycerol 15 g, catalyst weight 300 mg, 220 °C, 24 h.	[129]
Amberlyst 15	68%	Not indicate in figures	Investigation on etherification of glycerol and ethylene glycol with isobutylene using strong acid ion-exchange resins (Amberlyst 15 and 35) and two large-pore zeolites H-Y and H-Beta. The highest glycerol conversion 88.7% was achieved over zeolite H-Y after 8 h. The highest amount of TTBG was observed over A 35. The most appropriate temperature for etherification of glycerol and ethylene glycol is 60 °C.	[134]
Amberlyst 35	71%			
Zeolite H-beta	65%			
Zeolite H-Y	88.7%			
Pr-SBA-15	90%	MTBG: 9% DTBG: 56% TTBG: 35%	Acid catalyzed, etherification of bio-glycerol over sulfonic mesostructured silicas, 75 °C, 4 h.	[135]
Ar-SBA-15	100%	MTBG: 5% DTBG: 54% TTBG: 41%		
Alkaline earth metal oxides MgO, CaO, SrO, BaO	60%	Diglycerol + triglycerol: 90%	Glycerol etherification is carried out at 220 °C, in the presence of 2 wt% of catalyst, 20 h.	[63]
Ca _{1.6} Al _{0.4} La _{0.6} O ₃	91%	Diglycerol: 53.2% Triglycerol: 37.8%	Glycerol etherification is carried out at 250 °C, in the presence of 2 wt% of catalyst, 8 h.	[136]
Montmorillonite K-10 modified with LiOH (Clay Li/MK-10)	98%	Diglycerol: 53%	Glycerol etherification is carried out at 240 °C, in the presence of 2 wt% of catalyst, 12 h.	[137]
Hydrotalcite	77.7%	Diglycerol: 76% Triglycerol: 25%	Glycerol etherification is carried out at 240 °C, in the presence of 2 wt% of catalyst, 16 h.	[138]

(impregnating) the mesoporous solids with certain promoters [66]. However, even with the successful increase of conversion (94% in 24 h), significant formation of acrolein observed.

In another study on mesoporous materials, Clacens et al. [1] analyzed the different techniques for addition of several alkaline earth elements to mesoporous MCM-41, which include incorporation, impregnation and exchange. The best compromise between activity, selectivity, and catalyst leaching was observed with cesium impregnated on pure mesoporous silica presented. High selectivity of 90% to [di- + triglycerol] was obtained at a conversion rate of 80% over such catalysts.

As shown in Table 6, the optimum amount of catalyst used in glycerol etherification is around 2 wt%, although some reports that used higher catalyst reached 4 wt% [133]. Therefore, an increase in the catalyst amount does not necessarily lead to a better production yield, whereas an optimum amount is more favorable for the reaction. Thus, in that study, the optimum amount of catalyst was determined and used in the reaction process to study the effect of other parameters on the reaction.

The use of a suitable solid catalyst in etherification reactions that can replace the rather cumbersome homogeneous processes has been a subject of interest [65]. Using various solid catalysts, potential green catalytic production routes have been reported, with or without solvent. However, the high selectivity of DG at higher levels of glycerol conversion remains a challenge. Compared with homogeneous processes, heterogeneously catalyzed processes have slower

reaction rates [134]. Therefore, to improve the low reaction rates the reaction conditions of heterogeneous catalysis must be enhanced by increasing the reaction temperature and the amount of catalyst used. Another challenge that has to be addressed in heterogeneous processes is the dissolution of the active species into the reaction medium, which results in the partial homogeneity of the process. This phenomenon increases the difficulty in product separation and results in lower product quality, thus limiting the reusability of the catalyst [63]. Furthermore, preparing new catalysts with large porous frameworks is a challenging task because of the difficulty in controlling the resulting pore sizes and structures. In addition, large-pore catalyst materials will enhance mass transfer to overcome diffusion resistance [134].

4.4. Metal oxides as catalysts in etherification of glycerol

Metal oxide catalysts [111] have been used for etherification. The use of an alkaline binary metal oxide catalyst will produce a large amount of linear polyglycerols. Barrault et al. [66] studied the catalytic behavior of zeolitic and mesoporous catalysts with alkaline metals in glycerol etherification. Additionally, glycerol etherification over mesoporous materials, such as MCM-41 impregnated with metals, was studied. Clacens et al. [61,62] used mesoporous catalysts (MCM-41 type) and a Cs-ZSM5 catalyst for glycerol etherification. They observed that an increase in glycerol conversion resulted in loss of selectivity, which subsequently lowered the selectivity to DG.

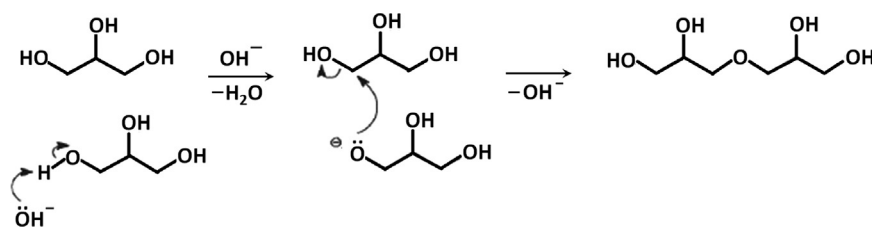


Fig. 10. Reaction scheme for the base-catalyzed glycerol etherification [63].

However, this increase in glycerol conversion increased the formation of triglycerol (TG). Ruppert et al. [63] investigated the use of CaO-based catalysts as heterogeneous catalysts in glycerol etherification to DG and TG. In addition, in the absence of a solvent, MgAl has been used in the formation of polyglycerols from glycerol [129].

Solid basic materials such as MgO, Al–Mg hydrotalcites, Cs-exchanged sepiolite, and mesoporous MCM-41 have been used as catalysts for glycerol transesterification with triglycerides. However, with MgO catalysts a glycerol/fat molar ratio of 12 at 240 °C was required to achieve a monoglyceride yield of 70% at a conversion rate of 97% [106,135]. Metal oxides such as MgO, CeO₂, La₂O₃, and ZnO have been used as solid base catalysts for the transesterification of glycerol with stoichiometric amounts of methyl stearate in the absence of solvent [88,121,136]. The catalysts were active, but the selectivity to mono-, di-, and triesters is similar to that obtained by homogeneous basic catalysts (40% monoester at 80% conversion).

Various microporous and mesoporous crystalline materials have been studied with and without different promoter elements [1,60,61,66]. Several modified zeolites and MCM-41-type mesoporous catalysts with different elements incorporated in their framework have also been investigated. Zeolites show severe limitations when involved large reactant molecules, especially in liquid-phase systems, which is frequently the case in the synthesis of fine chemicals. This observation is ascribed to the severe mass transfer limitations in the microporous solids. Microporous solids have a narrow and uniform micropore size distribution due to their crystallographically defined pore system. The reaction seems to have occurred mainly at the external surface of the catalyst; that is, the pore size of the modified zeolites was too small, which was one of the reasons behind the motivation in the preparation of basic mesoporous materials and the exchange or impregnation of basic elements. The impregnation method provides the most important activity, which is correlated with important active species incorporation. With regard to selectivity, mesoporous solids modified with cesium impregnation or exchanged with other substances lead to the best selectivity and yield to (di- + tri-) glycerol. The exchanged catalysts are most stable, and even if they are less stable, the impregnated catalysts can be reused without major modifications in their selectivity to the (di- + tri-) glycerol fraction.

With regard to microporous solids, Cs-exchanged X zeolites appeared to be active and selective catalysts, with glycerol conversion and (di- and tri-) glycerol selectivity of 79% and 95%, respectively, at a reaction temperature of 260 °C. By contrast, Cs-exchanged ZSM-5 materials proved to be less active. Using mesoporous MCM-41 catalysts loaded with Cs showed the most favorable results, which provided a (di- and tri-) glycerol selectivity of 97% at a conversion of 80% [61]. Clacens et al. [1] noted that the optimum results for catalyst leaching and stability were obtained using grafted solids that preserved their structure and specific area, properties which were not observed for their impregnated mesoporous catalysts. Finally, in the case of Mg- and La-containing mesoporous catalysts, the formation of acrolein due to the double dehydration as catalyzed by acid sites was found to

be significant. Thus, these catalysts were excluded as potential selective catalysts for the synthesis of di- and triglycerol [1,62].

Glycerol etherification reaction over alkaline earth metal oxides (BaO, SrO, CaO, and MgO) as promising heterogeneous catalysts with high activity has been studied. Previous studies have explored the catalytic potential of different CaO materials as examples of environmentally friendly and the most stable materials among the alkaline earth oxides [68]. By increasing glycerol conversion, the selective reaction that would yield the desired product should also be emphasized.

The additional criteria to be considered during the synthesis of heterogeneous catalysts include the availability of materials, ease of handling during preparation, affordability, thermal stability as measured by reusability, and regeneration. Moreover, developing and synthesizing heterogeneous catalysts that will bridge the gap created by the existing catalysts in terms of reusability are very important because they generate minimal leaching and are suitable for etherification reaction.

5. Mechanism of base-catalyzed etherification of glycerol

Oxidation and reduction occur at the same time during the etherification of glycerol, which includes the gain and loss of oxygen and hydrogen molecules between the hydroxyl group and glycerol. The mechanism of the etherification of glycerol using a basic catalyst has been studied by Ruppert et al. [63]. The mechanism includes two mechanistic schemes: deprotonation of the hydroxyl group and attack of the formed alkoxide anion on the carbon of the other glycerol molecule.

Surface properties, such as Lewis acidity, may perhaps have a role in the etherification of glycerol. As outlined in Fig. 10, it is difficult to explain the mechanism of a base-catalyzed etherification without the participation of the Lewis acid sites through the activation of a hydroxyl group as a leaving group [63]. Examples of such dual mechanism involving both basic and Lewis acid active sites have been reported for other heterogeneous catalytic reactions, for example, the destructive adsorption of chlorinated hydrocarbons on lanthanide oxide and oxide chloride materials [137,138].

In Fig. 10, when the basic condition provides adequate hydroxyl ions the reaction starts and one of hydroxyl groups in the glycerol molecule to be protonated. At that time, the protonated molecule of glycerol is ready to be combined with another molecule. Subsequently, the hydroxyl group of another molecule of glycerol is subjected to a nucleophilic attack of the protonated glycerol molecule. The formation of a water molecule after the attack properly recommends that the etherification reaction is a condensation reaction. Diglycerol molecule produces by the attack which combines two glycerol molecules into one longer molecule. Type of dimer produced is determined by the attachment point of one glycerol to another based on the positions of the primary and secondary hydroxyl groups.

6. Conclusions

Glycerol formation is equivalent to 10 wt% of the total biodiesel produced. Crude glycerol from biodiesel plant has low commercial value due to the presence of impurities of between 20% and 40%. In order to upgrade this low value product to the commercial grade, it should be purified through the costly refining process. Possible alternative technologies for the conversion of glycerol to value-added products are a subject of interest. Production of polyglycerols from glycerol provides interesting solutions to the problem as well as providing opportunities. Polyglycerols and their derivatives have vast applications in food, pharmaceutical and cosmetics industries. The most important product is diglycerol. Nature of the process, technical requirements and process behaviors of selective production of diglycerol and high oligomers through acid and base catalyzed processes are discussed in detail. Performance of different catalysts is reviewed and compared. Catalysts reported generally show diglycerol and triglycerol selectivities in the range of 50–80% and 20–40%, respectively at conversions values above 70%. An attempt to elucidate the reaction mechanism involved is also made. The mechanism is based on two mechanistic schemes i.e. deprotonation of the hydroxyl group and attack of the formed alkoxy anion on the carbon of the other glycerol molecule. The role of Lewis acid is also discussed in detail.

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